INTRODUCTION

Landfilling the municipal solids waste (MSW) is directly associated with the formation of leachate, i.e. wastewater generated generally by the substances dissolved in water percolating through the waste pile. This complex mixture contains several groups of hazardous substances, some in high concentrations, such as NH$_4$$. Some of them, like WWA, are found in trace concentrations, however, with very rich diversity of molecule construction. The quantity and quality of leachate depend of many factors, such as: landfill age, type of dumped waste, climate and hydrological conditions and adopted model of the installation operation. It is assumed that a single Mg of MSW containing 30–35% of moisture produces 0.05–0.07 Mg of leachate per year (Chai et al. 2013, Wang et al. 2016).

The treatment of leachate with biological methods (e.g. activated sludge or trickling filters) is widely used, primarily due to the low operating costs, and reduced environmental burden. However, these methods are usually not able to provide sufficient effectiveness removal of those organic substances that are resistant to biological degradation. That group of compounds rises in the later phases of the landfill biochemical evolution. Therefore, for the treatment of leachate generated on the landfills older than ≈ 10 years, the application of more costly physiochemical processes is proposed, such techniques are mentioned in literature data as coagulation and flocculation, adsorption on activated carbon, membrane filtration

ABSTRACT

The choice of the optimal method of municipal waste landfill leachate treatment should take into account such factors as: the variability of their composition and quantity over time, requirements for effluent or economic capacity. Due to the variety of compounds found in landfill leachate, it is advised to use a combination of different treatment processes. Biological methods are effective in the treatment of leachates from young landfills, but generally their efficiency declines significantly with the age of the landfill. Therefore, the physicochemical methods, i.e. advanced oxidation, adsorption, membrane methods or a combination of the mentioned, are preferred. The aim of the study was the assessment of the Fenton’s reagent utilization to process reverse osmosis concentrate of leachates collected from municipal non-hazardous waste landfill. The research was focused on the influence of pH on the process. Additionally, the effectiveness of organic compounds removal, increasing the biodegradability, as well as humic substances transformations were determined. The concentrations of humic compounds were measured by means of optical density at the wavelengths: 254, 265, 280, 320, 465 and 665 nm. In the experiment, the H$_2$O$_2$/Fe$^{2+}$ ratio was tested at with a dose of H$_2$O$_2$ equal to 3.4 g/l (0.1 M). It was found that the pH affects the efficiency of COD removal and the increase of the biodegradability of the landfill leachate retentate, as well as the removal of humic substances and its transformation. It was found that at pH 3, the highest removal of COD occurs, with simultaneous increase in biodegradability, and decrease of absorbance caused by humic compounds.

Keywords: AOP, Fenton’s reagent, RO retentate, landfill leachate

Influence of pH in AOP on Humic Compounds Removal from Municipal Landfill Leachate Concentrate after Reverse Osmosis

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or advanced oxidation (Jurczyk and Koc-Jurczyk 2017, Miklos et al. 2018). Among the membrane methods, the following are distinguished: micro-, ultra- and nanofiltration or reverse osmosis (RO) (Renou et al. 2008, Ince et al. 2010). However, one should pay attention to the fact that the above-mentioned methods are, in fact, not the methods of pollution disposal, because they do not lead to the degradation, in the meaning of changing the chemical structure of leachate component, but rather change their quantitative parameters, by reducing the volume of sum of the pollutant, but simultaneously, causing a proportional increase of the concentration. According to Wang et al. (2017), the RO retentate typically makes up 13 to 30% of the inflow volume. As a result, the effluent contains high concentrations of retained pollutants, obviously also including such high molecular mass compounds as humic substances. The main components of humic substances, occurring in the RO concentrate are humic (HA) and fulvic acids (FA), which constitute 61.7 to 75% of COD. Whilst the permeate can be discharged to a sewage system or utilized as technological water in landfill installation, the problem of highly loaded retentate rises along with time of operation. The most common treatment technology of concentrated leachate is recirculation on landfill; other technological solutions such as: solidification/stabilization, evaporation/distillation or advanced oxidation processes (AOPs), including Fenton’s reaction, are used less frequently.

The principles of Fenton’s reagent mechanism have been known for over a century, but were adapted as a technological method of wastewater disposal relatively recently, only in the 1990s (Huang et al. 1993). In this process, H₂O₂ is used as an oxidizer, Fe²⁺ as a catalyst, and the result of chemical reaction is formation of highly active radicals, according to equations 1 to 5 (Singh and Tang 2013), with hydroxyl radicals (OH⁻) recognized as main responsible for subsequent degradation of organic compounds.

\[
\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + \text{OH}^{-} + \text{OH}^{+} \quad (1) \\
\text{Fe}^{3+} + \text{H}_2\text{O}_2 & \rightarrow \text{HO}_2^{-} + \text{H}^{+} \quad (2) \\
\text{RH} + \text{OH}^{-} & \rightarrow \text{H}_2\text{O} + \text{R}^{+} \quad (3) \\
\text{OH}^{-} + \text{H}_2\text{O}_2 & \rightarrow \text{HO}_2^{-} + \text{H}_2\text{O} \quad (4) \\
\text{Fe}^{2+} + \text{OH}^{-} & \rightarrow \text{Fe}^{3+} + \text{OH}^{-} \quad (5)
\end{align*}
\]

In the presence of free radicals, the refractory organic compounds are efficiently mineralised or converted into biodegradable forms, which thereafter can be removed, for example, in subsequent biological processes. During violent reaction between Fenton’s reagent and compounds dissolved in leachate, molecules of high mass decrease mass, furthermore, complex aromatic or aliphatic hydrophobic chains are transformed to hydrophilic structures (Umar et al. 2010, Zhao et al. 2013, Koc-Jurczyk 2014). The effectiveness of the process depends on such conditions as: pH value, doses and molar ratios of Fe²⁺ and H₂O₂, as well as proportions of reactants to dissolved organic compounds (Fe²⁺/COD and H₂O₂/COD).

Since the products of RO are one of the major technological problems of landfill operation, a good solution is sought to efficiently dispose of, or, at least, significantly reduce its environmental impact. Thus, the aim of this study was an assessment of the chemical AOP effectiveness on the humic compounds removal from leachate concentrate generated in a technical scale RO installation. The influence of reaction environment pH on the efficiency of humic compounds removal was determined by measuring the optical density at a wavelength of \(\alpha = 254, 265, 280, 320, 465, 665\), and also, increase in the biodegradability expressed as a rise of COD/BOD index.

MATERIALS AND METHODS

Leachate sampling

The samples of leachate used in this study were collected from the landfill located in Subcarpathian Province, Poland, which has a status of regional instillation for municipal waste treatment (RIPOK) and is supplied by over 90 Gg of mixed municipal waste per year which are described, according to the Polish regulations, as “other than hazardous and inert, but with separated quarter for asbestos”. The landfill was operated since 1990 and during the sampling, it had an area of approximately 18 ha, including ten already closed quarters and a single active one.

The RO installation treats mixed effluent drained from the currently operated and recently closed quarters, with the daily outflow of about 30 m³/d. Before RO processing, the leachate is pre-filtered using bag filters to avoid the previously occurring frequent failures of membranes.
The effluent after RO concentrated in the ratio of approximately 1:3 was stored in a separate open-surface retention tank, from where it was re-circulated back to the waste pile. The characteristics of organic carbon contained in the RO’s retentate were based on such indicators as: chemical and biochemical oxygen demand, concentration of humic compounds and spectrometric determination which is shown in Table 1.

**Experimental procedure**

The AOP process was conducted under static conditions, in glass laboratory reactors with the capacity of 1 dm³ and constant temperature of 20°C. A *preri* presupposed values of pH were adjusted before oxidation by adding concentrated H₂SO₄. The Fenton’s reagents were dispensed once, directly to the reactor at the beginning of mixing phase, in order: firstly FeSO₄·x7H₂O, thereafter H₂O₂ as a 30% water solution. After 2h, to stop the reaction, pH was increased to 11 by 1M water solution of NaOH, this was followed by 0.5h of sedimentation phase, and after that the supernatant was sampled for analysis. The proportion of Fenton’s reagent based on previous experiences and was 1/10 (0.01 M Fe²⁺/0.1 M H₂O₂), and tested pH values ranged from 1 to 6. All analyses were performed at least in triplicate. In the supernatant samples, the concentration of humic compounds (Hermanowicz et al. 1999), organic substance expressed as COD (PN-ISO 6060:2006) and BOD₅ (DIN EN 26777) was determined. The optical properties of 1:10 solution in deionized water (SolPur), in the wavelength range SUVA 254, 265, 280, 320, 465 and 665 nm (Shimadzu) were measured in quartz cuvettes with a 1 cm optical path (Jena).

**RESULTS AND DISCUSSION**

The landfill site from which the samples were tested in this study, is well organized from the technical and operational point of view and has a well-developed infrastructure, also regarding installations for effective and safe drainage and collection of leachates.

A container-type compact leachate treatment plant, in which the RO process is carried out, operates on the landfill. In the concentration of leachates after RO, the average concentration of organic substances expressed as COD and BOD₅ was 26771 mg/l and 3750 mg/l, respectively, and the pH value was 6.49. After treatment of the condensate by advanced oxidation with Fenton’s reagent, in all series of tests, regardless of the initial pH value, the concentration of organic substances expressed as COD has decreased whilst BOD₅ increased, which may indicate the decomposition of high molecular mass organic substances into biodegradable, and simultaneous removal of organic substances. The extremes of the established pH values, as well the lowest and highest ones always resulted in higher concentrations of COD and lower BOD₅ after treatment. The efficiency of COD removal ranged from 6.6% (pH = 6) to 26.5% (pH = 3). Numerous literature data indicate an increase in the concentration of organic substances expressed as BOD₅ after the AOP’s wastewater treatment (Neyens and Baeyens 2003, Renou et al. 2008, Singh and Tang 2013, Miklos et al. 2018).

The highly reactive oxygen species formed during the Fenton’s reaction lead to the simplification of the chemical structure of complex organic compounds, which is the authors’ explanation for the observed decrease of COD, with the simultaneous increase in BOD₅. Zhao et al. (2013) and Singh and Tang (2013) report that high molecular weight organic substances can be effectively oxidized using the Fenton’s reagent. Zhao et al. (2013) report that the efficiency of COD removal from leachates is increasing along with the Fe²⁺/H₂O₂ proportion, and reaches the highest value, of 86 and 73.4% respectively, at a dose of Fe²⁺ of 2.24 and 0.56 g/l. Increasing the proportion of reagents to 1/10 caused a decrease in the efficiency of treatment, regardless of the dose of Fe²⁺ used. According to Singh and Thang (2013), the optimal molar ratio of Fe²⁺/H₂O₂ ranges from 2/5 to 1/100 (average 1/3) and, under these conditions, the efficiency of leachate treatment varies from 31 to 95%. In the case of raw leachates treatment, the proportion of Fe²⁺/H₂O₂ ranges between 2/5 and 1/60 and efficiency of purification 31–86%, respectively. The efficiency of leachate treatment by the Fenton’s process depends on the concentration of both reagents used. Although, as pointed by Sing and Tang (2013) hydrogen peroxide is still the main oxidant of refractive substances.

As a measure of biodegradability of organics in landfill leachate, the ratios of organic compounds referred to as BOD, and COD are assumed. Therefore, they are a crucial indicator
from the point of view of further leachate treatment using any of biological methods. The analyzed condensate from RO installation was characterized by a BZT/COD ratio of 0.14, which is quite high value as for leachate from municipal landfill. However, after the AOP treatment, the BOD/COD value was far higher, and reached the highest value of 0.33 at the pH = 3 (Fig. 1).

Humic compounds form a significant part of whole organic matter contained in landfill leachates, mainly derived from late phases of operation, but also in the products of landfill leachate treatment. In the examined condensate of leachates after RO (retentate), the content of humic compounds was 750 mg/l. The efficiency of humic compounds removal was the lowest at pH 6 (20%), whilst reaching 69% at pH 3. Analyzing the concentration of organic compounds (COD, BOD,) in relation to humic compounds, it was found that the concentration of humic acids decreased along with increasing COD concentration and BOD reduction (Fig. 2). The relationships between individual contamination indicators in the outflows from AOP reactor are shown in Figure 3.

A numerous group of organic compounds commonly found in natural environment, including surface waters, such as: HS, lignins, tannic acids or aromatic compounds, exhibit strong absorbance at a wavelength of 254 nm. On the other hand, this feature is not shown by such compounds as: esters, sugars, alcohols, saturated carboxylic acids and their derivatives, and many others. It is widely accepted that the absorbance at 280 nm (A280) results from the content of alkaline lignin-like compounds; hence, higher A280 values would indicate the presence of compounds that are difficult to humify (Helms et al. 2008). The absorbance value A465 reflects the content of the compounds that are characteristic for the initial stage of degradation of biomass gathered in the waste pile, because it is positively correlated with the amount of “young” forms of humic acids that are formed at an early stage of transformation of organic matter. In turn, the values of A665 enable to determine the content of substances characterized by high level of humification (Chmiel 2009).

While analyzing Figure 4 that shows the changes in the content of organic compounds and the optical density of leachate solutions in outflows from reactors of different pH, it can be noted that the decrease of COD concentration, like an increase of BOD, is accompanied by decreasing absorbance, which is particularly evident in the ranges of intermediate and near ultraviolet; from

### Table 1. Organic compounds concentration indicators in reverse osmosis-derived concentrate: COD, BOD, sum of humic substances and values of absorbance at selected wavelengths

<table>
<thead>
<tr>
<th>COD [mg/l]</th>
<th>BOD₅ [mg/l]</th>
<th>Humic compounds [mg/l]</th>
<th>A₂₅₄</th>
<th>A₃₈₀</th>
<th>A₄₁₀</th>
<th>A₄₆₅</th>
<th>A₆₆₅</th>
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<td>26771</td>
<td>3750</td>
<td>750</td>
<td>75.6</td>
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![Figure 1](image.png)

Figure 1. Ratio of BOD₅ to COD in reverse osmosis retentate after the AOP treatment
Figure 2. Changes in concentrations of organic compounds (COD, BOD₅), including humic compounds in reverse osmosis-derived retentate treated by chemical advanced oxidation with Fenton’s reagent.

Figure 3. The relationships between analyzed parameters of organic carbon and the content of humic compounds in outflows after chemical oxidation of RO concentrate.
254 to 320 nm, less in the visible blue and yellow band. In the case of the substances determined at a wavelength of 665 nm, an increase of the absorbance comparing to the retentate from reverse osmosis was observed. Moreover, while analyzing the remaining absorbance readings, it was found that reaction conducted at pH 3 results in the highest removal efficiency of compounds measured at 465 nm (78%), and the lowest at 254 and 265 nm (44%). Both lowering and raising the pH, resulted in a decrease of the removal effectiveness of all the above-mentioned light absorbers.

As it is apparent from the foregoing reasoning, the A2/4 and A4/6 coefficients are practicable parameters that would be used to assess the advancement of the humification process in waste bed. Young humic acids are characterized by higher values of these coefficients in comparison with those highly humified. In this study, a reduction of COD concentration occurred simultaneously with an increase of the A2/4 ratio, and a slight increase in the A4/6 ratio was observed (Fig. 5).

According to Chen et al. (2002), higher A2/4 ratios are mainly due to the absorption by C=O functional groups, when the lower would be a result of the absorption by aromatic C=C functional groups, especially those characterized by high condensation of aromatic rings as well as high molecular weight. In our studies, the highest value of the A2/4 ratio was observed at pH 3, both lowering and increasing the pH resulted in a decrease in A2/4 ratios. Only at pH 6, the reduction of as much as 80.7% was observed. As it follows, the Fenton’s reagent at pH-values ranges 1–5 could break down the compounds containing highly condensed aromatic rings.

The A4/6 ratio enables to estimate the general character of HS. Quotient A4/6 should be treat-

![Figure 4](image-url)  
**Figure 4.** Changes in concentrations of organic compounds (COD, BOD₅), including humic substances (deferent optical density) in reverse osmosis-derived retentate treated by chemical advanced oxidation with Fenton’s reagent

![Figure 5](image-url)  
**Figure 5.** Changes in concentrations of organic compounds (COD, BOD₅) and A2/4 and A4/6 ratio
ed as a humification indicator. Thus, the degree of HS humification can be determined from the inspection of optical density curves. The higher the optical density, the greater the amount of humic acids, characterized by high optical density. The ratio of A4/6 for humic acids is usually less than 5.0, while for fulvic acids it ranges between 6.0 and 8.5. It is assumed that the value of the A4/6 index drops along with the increase of the molecular weight of humic compounds, or with the increase of polymerization of their aromatic nucleus. In this investigation, it was found that during the reaction conducted at pH 6 it was 10.6, while in the effluent after reverse osmosis – 14.18. Acidification of leachates up to pH 1–5 resulted in a reduction of the A4/6 quotient below 5. As result of the above-mentioned considerations it can be assumed that the Fenton’s reaction at low pH contributes to increase of carbon atoms number, and the decrees of oxygen content in their structure. For this reason, the A4/6 ratio can be used as an indicator of humification. Figure 6 shows the relationship between individual, above-mentioned coefficients (Chen et al. 2002).

The transformations of humic substances are closely related to the degradation of organic substances. It can be inferred that the hardly degradable fractions are directly degraded to easier degradable fractions after the oxidation process (Wang et al. 2017). Garcia et al. (1996) investigated the oxidation of humic substances and found 110 different non-humic organic compounds as products of degradation, such as carboxylic acids, hydrocarbons, aldehydes, ketones and furancarboxylics acids.

CONCLUSIONS

The Fenton’s reaction, it is still a rare solution for treatment difficult wastewater such as a leachate, coming from landfills with different operational lifetime, although its mechanism has been known for many years, the installation design is extremely simple, and both investment and operating costs are not the highest, assuming high efficiency of organic compounds removal and significant increase in biodegradability. Moreover, as this research indicates, it can also be utilized to improve the process of disposal of membrane filtration-derived concentrates. In the case of retentate treated in this work, maintaining the pH of the AOP reaction at the level of 3 resulted in the highest BOD5/COD ratio, as well as the lowest optical density at all electromagnetic wavelengths analyzed, and also the lowest ratio of A4/6, and the highest A2/4. In fact, the control over the proper hydrogen ions concentration in reaction environment, which has a crucial role for the effectiveness of process, could be the most important operational hindrance.

REFERENCES